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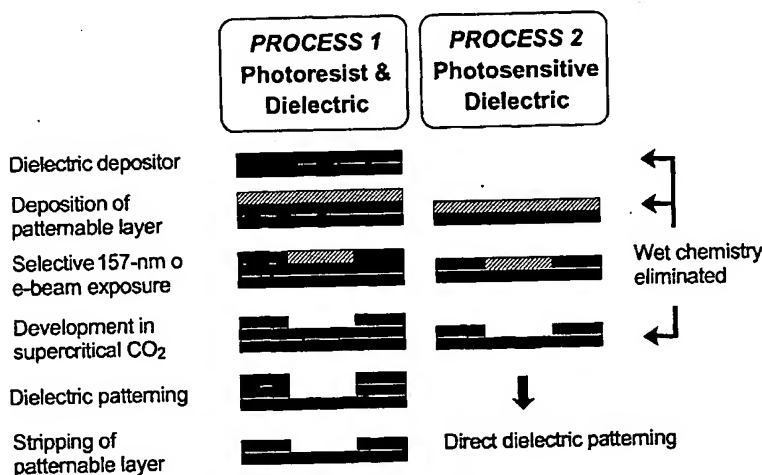
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(54) Title: **SOLVENTLESS, RESISTLESS DIRECT DIELECTRIC PATTERNING**



(57) Abstract: Provided is a process for lithographically patterning a material on a substrate comprising the steps of (a) depositing a radiation sensitive material on the substrate by chemical vapor deposition; (b) selectively exposing the radiation sensitive material to radiation to form a pattern; and (c) developing the pattern using a supercritical fluid (SCF) as a developer. Also disclosed is a microstructure formed by the foregoing process. Also disclosed is a process for lithographically patterning a material on a substrate wherein after steps (a) and (b) above, the pattern is developed using a dry plasma etch. Also disclosed is a microstructure comprising a substrate; and a patterned dielectric layer, wherein the patterned dielectric layer comprises at least one two-dimensional feature having a dimensional tolerance more precise than 7%. Also disclosed is a microelectronic structure comprising a substrate; a plurality of transistors formed on the substrate; and a plurality of conductive features formed within a dielectric pattern, wherein the plurality of conductive features include at least one two-dimensional feature having a dimensional tolerance more precise than 7%.



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

SOLVENTLESS, RESISTLESS DIRECT DIELECTRIC PATTERNING

5 STATEMENT AS TO RIGHTS TO INVENTIONS MADE UNDER FEDERALLY SPONSORED RESEARCH AND DEVELOPMENT

This invention was made in the course of research sponsored in part by the National Science Foundation. The U.S. Government may have certain rights in this invention.

10 FIELD OF THE INVENTION

This invention relates to methods of lithographic patterning using solvent-free compositions. The invention also relates to direct patterning without resists.

BACKGROUND OF THE INVENTION

Current lithographic processes employed by the microelectronics industry
15 have significant environmental, safety and health (ESH) impacts. The fabrication of semiconductor devices uses photoresist to lithographically define features at every mask level. Advanced complementary metal oxide semiconductor (CMOS) and bipolar integrated circuit (IC) processes can require in excess of twenty-five mask levels. This large number of processing steps results in significant volumes of chemicals being
20 consumed. Wet solutions are used for the application of the photoresist layer and during the development step. Thus, improved resist processing presents a clear need and an opportunity to reduce the ESH impact of microelectronics manufacturing. The present invention fulfills this and other needs.

25 SUMMARY OF THE INVENTION

The present invention relates to a process for lithographically patterning a material on a substrate comprising the steps of:

- (a) depositing a radiation sensitive material on the substrate by chemical
vapor deposition;
- 30 (b) selectively exposing the radiation sensitive material to radiation to
form a pattern; and
- (c) developing the pattern using a supercritical fluid (SCF) as a developer.

The present invention also relates to microstructures formed by the foregoing process.

The present invention also relates to a process for lithographically patterning a material on a substrate wherein after steps (a) and (b) above, the pattern is developed using a dry plasma etch.

The present invention also relates to a microelectronic structure comprising a substrate; and a patterned dielectric layer, wherein the patterned dielectric layer comprises at least one two-dimensional feature having a dimensional tolerance more precise than 7% of dimension of the two-dimensional feature.

The present invention also relates to a microelectronic structure comprising a substrate; a plurality of transistors formed on the substrate; and a plurality of conductive features formed within a dielectric pattern, wherein the plurality of conductive features include at least one two-dimensional feature having a dimensional tolerance more precise than 7% of the dimension of the two-dimensional feature.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a comparison of a conventional process employing a sacrificial photosensitive resist layer with one using direct dielectric patterning.

Figures 2A and 2B show atomic force micrograph of electron-beam patterned fluorocarbon films. Figure 2A shows the pattern before development with supercritical CO₂ and figure 2B after development.

DESCRIPTION OF THE SPECIFIC EMBODIMENTS

Conventional photoresists are applied by spin-on technology. Typically, only a few percent of the material that is dispensed onto the silicon wafer actually becomes the photoresist layer and the rest becomes waste (1). The waste solution typically contains polymeric matrix material, photosensitive agents and solvents. Thus, spin-on resists result in large volumes of waste material, which require safe and costly disposal. The resist solutions are usually combustible, so the materials are held at temperatures below their flash point (2). Also, spin-on processes pose potential risks for worker exposure to solvents. Regulatory constraints on volatile organic chemical (VOC) emissions have motivated efforts to design revolutionary processes (3). Thus the use of vapor deposition processes and the use of supercritical carbon dioxide (SCF CO₂) as developer may provide critical alternatives to the present solvent-based approaches.

After optical exposure, the pattern in a photoresist layer must be developed. As critical feature size diminishes, the selectivity and environmental friendliness of the solvent used as the developer becomes increasingly important. Suitable alternative solvents with very high selectivity and adjustable solvating power are therefore required. The application of liquid developers in the mainstream production environment generates enormous waste streams causing great environmental concern. These properties are not adequately addressed by the aqueous base solutions currently in use. Thus again there are potential opportunities in using such liquids as SCF CO₂, not only for environmental reasons but because simple adjustment of pressure and/or temperature can provide a means of optimizing solvent behavior.

Environmental and economic driving forces also favor reducing the number of processing steps required for IC production. This could be achieved by combining the functionality of photosensitive and low dielectric constant thin films. Fluoropolymers and organosilicon films (both types of polymers being soluble in SCF CO₂) have low dielectric constants and good thermal stability, desirable characteristics for future interconnect insulating materials. If the patterned photoresist layer can be imaged and also satisfy the requirements for low dielectric constant interlevel dielectric materials, a great number of processing steps would be eliminated.

The first step in the present process for lithographically patterning a material on a substrate involves depositing a radiation sensitive material on the substrate by chemical vapor deposition (CVD). Thus no organic solvent is used during resist deposition. CVD includes pulsed plasma enhanced chemical vapor deposition (PECVD) and pyrolytic CVD as well as continuous PECVD.

Plasma polymerization is a common method for depositing fluorocarbon and organosilicon thin films (1,2). The fluorocarbon polymers and organosilicon films comprise the radiation sensitive materials of the present invention. PECVD uses continuous radio frequency (rf) power to excite the precursor gases in order to deposit films within the glow discharge region. The resulting plasma contains ions, radicals, excited species and neutrals from which solid coatings are deposited.

With pulsed PECVD and pyrolytic CVD methods, the as-deposited films are anticipated to have fewer crosslinking sites than their continuous PECVD counterparts. Thus, irradiation resulting in the production of cross-linking groups can result in dramatic differences in chemical structure. Increasing structural differences between the as-deposited and irradiated films should correlate to higher photolithographic

contrast. In addition, growth rates for the pyrolytic processes are very high, which is a desirable feature for commercialization.

Pulsed PECVD limits the duration of plasma excitation and thus affords a degree of control over the reaction pathways available to the feed gas. The concentrations of species under these dynamic conditions can be very different than those achieved at steady state. In addition, plasma damage of the growing films by ion bombardment and UV irradiation is reduced. Reasonable film growth rates can be maintained because deposition continues after the plasma is extinguished.

Pyrolytic CVD of fluorocarbon has previously been reported (4). In this process, decomposition of the feed gas occurs over a hot filament or plate in vacuum, while the growth substrate is maintained around room temperature. The pyrolytic process, involves a different, and presumably less complex, reaction network than a plasma process.

As used herein, the phrase "radiation sensitive material" refers to any polymer, or other film-forming material that becomes a resist or any composition that can be induced to etch, vaporize or ion implant to form a pattern. The term "radiation" includes thermal radiation as well as photonic radiation, including radiation from particle beam sources (such as electron beam, ion beam) as well as other types of electromagnetic radiation.

In one embodiment, the radiation sensitive material of the present invention have low dielectric constants, typically less than 3.0. In one embodiment, the dielectric constant ranges from 1.9 to 2.7.

In one embodiment, the radiation-sensitive material of this invention is a fluorocarbon polymer. In one embodiment, the fluorocarbon polymer of this invention is poly(CF₂) which is made by the polymerization of the reactive diradical difluorocarbene (:CF₂) (5). Hexafluoropropylene oxide (HFPO) is used as a thermal source of the radical difluorocarbene (:CF₂) (5). While not wishing to be bound by theory, it is believed that the unimolecular pyrolytic decomposition of HFPO proceeds according to the following scheme:

Scheme 1



ESH impact of a CVD process can be minimized through the design of the deposition chemistry. This design involves several steps. The first is selection of CVD precursor gases which are as benign as possible. In addition, known primary reaction pathways of these precursors should not result in hazardous effluents. Next, reactor conditions can be found which efficiently react gas to form film. These steps minimize material and energy utilization as well as effluent gas production.

In one embodiment, the radiation sensitive material is an organosilicon film. The production of organosilicon films by pyrolytic CVD has been previously reported (6). Growth rates of this type of film deposition are high (well over 3,000 Å/min). High deposition rates increase throughput and reduce cost. Fast growth rates also minimize chemical consumption and effluent.

The organosilicon films of the present invention include organosilanes and organosiloxanes. Examples of organosilanes include without limitation tetraethylorthosilicate, diethylsilane, tetramethylsilane and triethoxysilane. In one preferred embodiment, the organosilicon film used as the radiation-sensitive material is derived from hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane or a mixture thereof. Polyorganosiloxanes can also be deposited by pyrolytic CVD. Methods of forming a silicon oxide film on a heated substrate by chemical vapor deposition (CVD) using an organosilicon compound gas and oxygen gas are disclosed in U.S. Patent 5,593,741. The use of vapor deposited organosilicon compounds as a dry resist is described in U.S. Patent 5,439,780. The fluoropolymers and organosilicon films of the present invention allow for direct dielectric patterning.

In one embodiment, a photoacid generator is included in the first step of the present process, namely the depositing of radiation sensitive material on the substrate by CVD. Upon exposure to radiation, the photoacid generator generates an acid. Suitable acid generators include triflates (e.g., triphenylsulfonium triflate or bis-(t-butyl phenyl) iodonium triflate), pyrogallol (e.g., trimesylate of pyrogallol), onium salts such as triarylsulfonium and diaryl iodonium hexafluorantimonates, hexafluoroarsenates, trifluoromethane sulfonates, perfluoro alkyl sulfonium iodonium salts, and others; trifluoromethanesulfonate esters of hydroxyimides, alpha-alpha'-bis-sulfonyl diazomethanes, sulfonate esters of nitro-substituted benzyl alcohols and naphthoquinone-4-diazides and alkyl disulfones. Other suitable photoacid generators are disclosed U.S. patent 4,491,628 and 5,071,730.

The second step of the process involves exposing the radiation sensitive material to radiation to form a pattern. The radiation used to irradiate the radiation sensitive material includes ultraviolet radiation, deep ultraviolet radiation, extreme-ultraviolet radiation (soft x-rays), the radiation corresponding to the gap between soft x-rays and deep ultraviolet radiation, x-rays, electron beam, and ion beam radiation. In one embodiment, the wavelength of the deep uv radiation ranges from 120 nm to 450 nm, and in one embodiment 157 nm, in one embodiment 193 nm, and in embodiment 246 nm.

The third step involves developing the pattern using a supercritical fluid (SCF) as a developer. A SCF is defined as any fluid at a temperature that is greater than its critical temperature and at a pressure that is greater than its critical pressure. Photography using aqueous base development has become the workhorse of the electronics industry. Any developer that replaces aqueous base should provide superior images than possible with today's resist materials. Using current processes, there has been remarkable progress in the miniaturization of electronic devices over the last 2-3 decades. The trend in the electronics industry toward miniaturization and increased complexity of the IC's demands tremendous improvement both in the chemistry of the resists as well as in their processing. This has put tremendous pressure on resist design and developer usage. As target dimensions continue to decrease, the selectivity of the developer becomes increasingly important in achieving high-resolution features. Solvents with such selectivity include supercritical fluids (SCF), unusual solvents with many characteristics not found in conventional liquids. The unique properties of these fluids include liquid-like densities, gas-like diffusivities and viscosities, negligible surface tension and pressure adjustable solvating power (7). Suitable examples of supercritical fluids include carbon dioxide; mixtures of carbon dioxide with at least one of butane, pentane, toluene, cyclohexane, acetonitrile, and methanol; 2,3-dimethylbutane; ethanol; n-hexane; propane; propane/water mixtures; sulfur hexafluoride; propane; and ethane. In one preferable embodiment, the supercritical fluid is supercritical carbon dioxide (SCF CO₂), owing to its nontoxic, nonflammable nature and very low cost. Using SCF CO₂ as a developer eliminates much waste as is involved with using traditional aqueous base developers.

Along with being an extremely selective solvent, it is considered to be an "environmentally responsible" solvent both because it is not ozone depleting and due in part to its ability to be recycled by simple compression-decompression steps. Presently, millions of gallons of wastewater from semiconductor processing facilities are treated

annually. Supercritical solvents offer the possibility of superior developer performance and simpler disposal or recycling with less effort and expenditure of energy than current solvents.

In one embodiment of the present invention, the step of developing the pattern is performed using a dry plasma etch, instead of SCF CO₂. The basic technique of plasma etching will be well known to those skilled in the art. A glow discharge is used to produce chemically reactive species (atoms, radicals and ions) from a relatively inert molecular gas. The etching gas is selected so as to generate species which react chemically with the material to be etched, and whose reaction product with the etched material is volatile.

The substrates for the present process include patternable substrate such as ceramic materials (such as glass), epoxy materials, plastic materials, semiconductor materials (such as silicon on semiconductor), silicon wafers, magnetic discs, and printed circuit boards.

The present process for lithographic patterning encompasses both direct dielectric patterning as well as patterning with a resist. The direct dielectric patterning process is a resistless process wherein the patterned layer is used as an imagable dielectric in which the patterned layer remains as part of the device rather than being a sacrificial resist layer which is stripped away. The conventional patterning process uses the patterned layer as a resist, and this pattern is transferred to an underlying layer by etching and then stripping away the resist. Thus in a conventional process that uses a resist, the substrate comprises an underlying dielectric layer and a sacrificial resist layer on top of the underlying dielectric layer. Fig. 1 illustrates the comparison of the conventional process with the direct patterning process. The conventional scheme employs a sacrificial photoresist layer to pattern the dielectric layer. In the direct dielectric patterning process reduces the number of processing steps by using a photosensitive dielectric. The simplicity of the direct patterning process is favored by both environmental and economic factors. Also indicated in Figure 1 are steps in which the CVD and SCF CO₂ can replace solution-based processes.

In one embodiment of the present invention, the pattern on the substrate formed by the direct dielectric patterning process is superior to a conventional process that does not use direct dielectric patterning. This is likely the result of fewer processing steps (see Figure 1), and an additional step is likely to introduce added distortions. As such, the line geometries, resolution, dimensional tolerance, and/or the aspect ratio

(height/width) of the patterns formed on the substrate are superior to those that be provided by a conventional technique that does not utilize direct dielectric patterning.

Thus, in one embodiment, the present invention provides a microstructure comprising a substrate and a patterned dielectric layer which comprises at least one two dimensional feature having a dimensional tolerance more precise than 7%, preferably more precise than 6%. Furthermore, when scaling a technology, it becomes increasingly difficult to sustain a constant dimensional tolerance as feature sizes are correspondingly reduced. Hence, it is advantageous to even maintain a dimensional tolerance at a level of 7-8%, as dimensional tolerance tends to worsen (i.e., becomes less precise) with decreasing dimensions. As used herein, "microstructure" includes any structure that can be created using integrated circuit technology including traditional electronic and microelectronic (including microelectromechanical) systems as well as combinations of the two systems. Thus, "microstructure" is inclusive of "microelectronic" structure which latter is produced by a microelectronic system.

"Dimensional tolerance" here refers to the dimensional precision in production of the microstructure. Thus, for example, a 180 nm structure having a dimensional tolerance of plus or minus 14 nm would have a dimensional tolerance in percent of $(\pm 14/180)$ times 100 or $\pm 7.78\%$ of the featured dimension. A "more precise" dimensional tolerance (higher precision) indicates a lower percentage number, i.e., lower than 7.78% of the featured dimension. While not wishing to be bound by theory, it is believed that the better dimensional tolerance and higher aspect ratio of the two dimensional features produced by the direct dielectric patterning process of the present invention over conventional process is due to the lower surface tension of SCF CO_2 which does not allow the microstructures to collapse and topple as readily as microstructures produced by the conventional process (which is not a direct dielectric process, but where images are transferred through a sacrificial resist layer as disclosed above). With regard to aspect ratios, it is believed that the conventional process can yield microstructures with a maximum aspect ratio of (4-5):1. However with direct dielectric patterning one can obtain microstructures with improved aspect ratios, preferably greater than 5:1 ratios. Furthermore, when scaling a technology, it becomes increasingly difficult to sustain a constant aspect ratio for dimensional tolerance as nanoscale structures become increasingly more fragile and more vulnerable to fluid forces and dynamics.

In one embodiment, the microelectronic structure comprises conductive features. For example, conductive features such as transistors and metal lines may be formed by metallic deposition within the dielectric pattern as part of a process for forming transistors on the substrate.

5 As can be seen from Figure 1, on the left the conventional process employs a sacrificial photosensitive resist layer to pattern the dielectric layer. On the right, the number of steps is drastically reduced by use of a photosensitive dielectric. Such process simplicity is favored by both environmental and economic factors. The arrows on the right indicate steps in which the CVD and SCF CO₂ can replace solution based processes
10 (wet chemistry).

The present invention also provides for a three-dimensional structure formed on a substrate. The three-dimensional structure is formed by a three-dimensional direct patterning process. Current lithographic processes, such as two photon patterning and holographic imaging enable the transfer of complex three dimensional structures into
15 a resist film. However, this ability to write three dimensional structure in the resist is lost when the image is transferred into the etched substrate, as only a two dimensional mapping is transferred during the etching process. However, the present invention provides for the imaging of a three dimensional structure on the substrate, as it is not limited to a secondary transfer of an image or structure through a resist layer which only
20 allows two-dimensional mapping. Thus the direct patterning process of the present invention allows the formation of a three-dimensional structure on a substrate.

As mentioned above, a three dimensional imaging technique can be use to selectively expose a radiation sensitive dielectric material to radiation. Examples of such imaging technique include multi-photon patterning and holographic imaging.

25 The production of three-dimensional sensible objects by multi-photon patterning is disclosed in U.S. Patent 4,288,861. By "multiphoton", it is meant to refer to the coincidence or intersection of at least two beams of electromagnetic radiation at a target location in a molecule with sufficient incident energy to effect a selected change of energy level within the molecule as by photon absorption.

30 The use of holographic imaging in lithographic processes is well known to those or ordinary skill in the art. Methods for defining three-dimensional structure of an object using holographic imaging are disclosed in U.S. Patents 5,937,318; 5,910,660 and 5,640,255.

Figures 2A and 2B show atomic force micrograph of electron-beam (e-beam) patterned fluorocarbon films. Figure 2A shows the pattern produced by e-beam radiation before development with SCF CO₂. The figure shows densification or volatilization. Figure 2B shows the pattern after development with SCF CO₂ and shows substantially removal of the material deposited by CVD (which was a fluorocarbon derived from hexafluoropropylene oxide (HFPO)) from the exposed regions.

Each of the documents referred to in this application is incorporated herein in its entirety and for all purposes by reference. Unless explicitly indicated to the contrary, all numerical quantities in this description specifying amounts of materials, number of carbon atoms, and the like, are to be understood as modified by the word "about."

While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

REFERENCES

1. Campbell, S.A., *The Science and Engineering of Microelectronic Fabrication*. 1996: Oxford University Press.
2. Wolf, S. and R.N. Tauber, *Silicon Processing for the VLSI Era: Volume 1-Process Technology*. 1986: Lattice Press.
3. Nalamasu, O., T.I. Wallow, F.M. Houlihan, E. Reichmanis, A.G. Timko, G. Dabbagh, R.A. Cirelli, R.S. Hutton, and N.E. November, *Recent Progress in Resist Materials for 193 nm Lithography*, Future Fab International, 1997. 1(2): p. 159.
4. Limb, S.J., C.B. Labelle, K.K. Gleason, D.J. Edell, and E.F. Gleason, *Growth of fluorocarbon polymer thin films with high CF₂ fractions and low dangling bond concentrations by thermal CVD*. Appl. Phys. Lett., 1996. 68: p. 2810.
5. Knickelbein, M.B., D.A. Webb, and E.R. Grant, *New Devices for the Production of Intense Pulsed Jets of CF₂: Laser Spectroscopic Characterization*. Mater. Res. Soc. Proc., 1985. 38: p. 23.
6. Kwan, M.C. and K.K. Gleason, *Pyrolytic CVD of Poly(organosiloxane) Thin Films*. Adv. Mater. : Chem. Vap. Deposition, 1997. 3(6): p. 299.
7. McHugh, M.A. and Krukoni, V.J., *Supercritical Fluid Extraction: Principles and Practice*, 2nd ed., Butterworth-Heinemann, Stoneham, MA 1994.

WHAT IS CLAIMED IS:

- 1 1. A process for lithographically patterning a material on a substrate
2 comprising the steps of:
3 (a) depositing a radiation sensitive material on the substrate by chemical
4 vapor deposition;
5 (b) selectively exposing the radiation sensitive material to radiation to
6 form a pattern; and
7 (c) developing the pattern using a supercritical fluid (SCF) as a developer.
- 1 2. The process of claim 1 that is a direct dielectric patterning process.
- 1 3. The process of claim 1 wherein the substrate comprises an
2 underlying dielectric layer and a sacrificial resist layer on top of the underlying dielectric
3 layer.
- 1 4. The process of claim 1 wherein the radiation sensitive material
2 after selective exposure to radiation results in a positive-type resist.
- 1 5. The process of claim 1 wherein the radiation sensitive material
2 after selective exposure to radiation results in a negative-type resist.
- 1 6. The process of claim 3 further comprising the step of transferring
2 the pattern from the sacrificial resist layer to the underlying dielectric layer by etching,
3 and stripping away the sacrificial resist layer.
- 1 7. The process of claim 1 further comprising the step of:
2 including a photoacid generator in step (a).
- 1 8. The process of claim 1 wherein the chemical vapor deposition
2 comprises pyrolytic chemical vapor deposition.
- 1 9. The process of claim 1 wherein the radiation sensitive material has
2 dielectric constant of less than about 3.0.
- 1 10. The process of claim 1 wherein the dielectric constant of the
2 radiation sensitive material ranges from about 1.9 to about 2.7.

- 1 11. The process of claim 1 wherein the radiation sensitive material is
2 selected from the group consisting of a fluorocarbon and an organosilicon compound.
- 1 12. The process of claim 11 wherein the fluorocarbon comprises
2 poly(CF₂).
- 1 13. The process of claim 12 wherein the poly(CF₂) is made by
2 polymerization of difluorocarbene (:CF₂).
- 1 14. The process of claim 13 wherein the difluorocarbene is derived
2 from hexafluoropropylene oxide.
- 1 15. The process of claim 11 wherein the organosilicon compound is
2 selected from the group consisting of organosilanes and organosiloxanes.
- 1 16. The process of claim 11 wherein the organosilicon compound is
2 derived from at least one member selected from the group consisting of
3 hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane.
- 1 17. The process of claim 1 wherein the radiation used to form the
2 pattern is selected from the group consisting of deep ultraviolet radiation (DUV), extreme
3 ultraviolet radiation, ultraviolet radiation (UV), and x-rays and ion beam.
- 1 18. The process of claim 1 wherein the radiation used to form the
2 pattern is electron beam radiation.
- 1 19. The process of claim 17 wherein the wavelength of the deep
2 ultraviolet radiation is a member selected from the group consisting of 193 nm and 157
3 nm.
- 1 20. The process of claim 1 wherein the supercritical fluid (SCF) is
2 supercritical carbon dioxide.
- 1 21. The process of claim 1 wherein the supercritical fluid (SCF) is a
2 mixture of carbon dioxide and at least one member selected from the group consisting of
3 propane, butane, 2,3-dimethylbutane, pentane, toluene, n-hexane, cyclohexane,
4 acetonitrile, methanol, and ethanol.

- 1 22. The process of claim 1 wherein the substrate is a semiconductor
2 substrate.
- 1 23. The process of claim 1 wherein the substrate is a silicon wafer.
- 1 24. The process of claim 1 wherein the substrate comprises an epoxy
2 material, a ceramic material, a magnetic disc, or a printed circuit board.
- 1 25. A process for lithographically patterning a material on a substrate
2 comprising the steps of:
3 depositing a radiation sensitive material on the substrate by chemical vapor
4 deposition;
5 selectively exposing the radiation sensitive material to radiation to form a
6 pattern; and
7 developing the pattern using a dry plasma etch.
- 1 26. A microstructure formed by a process comprising the steps of :
2 depositing a radiation sensitive material on a substrate by chemical vapor
3 deposition;
4 selectively exposing the radiation sensitive material to radiation to form a
5 pattern; and
6 developing the pattern using a supercritical fluid (SCF) as a developer to
7 form the microstructure; wherein the process is direct dielectric patterning process.
- 1 27. A microstructure comprising:
2 a substrate; and
3 a patterned dielectric layer, wherein the patterned dielectric layer
4 comprises at least one two-dimensional feature having a dimensional tolerance more
5 precise than 7% of the dimension of the two-dimensional feature.
- 1 28. The microstructure of claim 27 wherein the patterned dielectric
2 layer is formed by a direct patterning process.
- 1 29. The microstructure of claim 28 wherein the direct patterning
2 process comprises depositing a radiation sensitive dielectric material on said substrate and
3 selectively exposing the radiation sensitive dielectric material to radiation.

1 30. The microstructure of claim 27, wherein the patterned dielectric
2 layer is formed by a solventless lithographic process.

1 31. The microstructure of claim 30, wherein the solventless
2 lithographic process comprises using a supercritical fluid as a developer.

1 32. A microelectronic structure comprising:
2 a substrate;
3 at least one transistor formed on the substrate; and
4 at least one conductive two-dimensional feature formed within a
5 dielectric pattern, wherein the conductive two-dimensional feature has a dimensional
6 tolerance more precise than 7% of the dimension of the two-dimensional feature..

1 33. The microelectronic structure of claim 32, wherein the conductive
2 feature further includes a plurality of transistors.

1 34. The microelectronic structure of claim 32 wherein the conductive
2 feature comprise at least one metal line.

1 35. A microstructure comprising:
2 a substrate; and
3 a three-dimensional structure formed on the substrate, wherein the
4 three dimensional structure is formed by a three-dimensional direct patterning process.

1 36. The microstructure of claim 35 wherein the three-dimensional
2 direct patterning process comprises depositing a radiation sensitive dielectric material on
3 the substrate and selectively exposing the radiation sensitive dielectric material to
4 radiation using a three-dimensional imaging technique.

1 37. The microstructure of claim 36 wherein the three-dimensional
2 direct patterning process further comprises using a supercritical fluid as a developer.

1 38. The microstructure of claim 36 wherein the three-dimensional
2 imaging technique comprises two-photon patterning.

1 39. The microstructure of claim 36 wherein the three-dimensional
2 imaging technique comprises holographic imaging.

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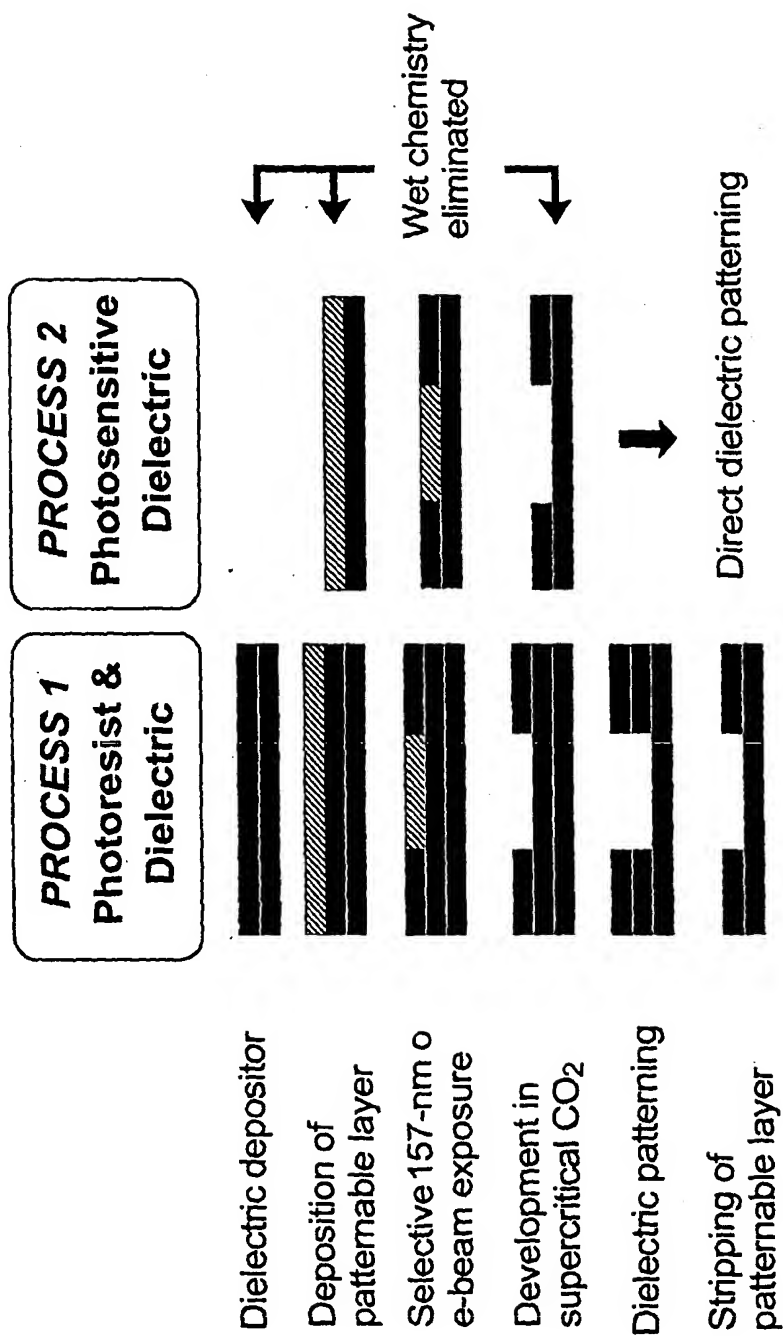
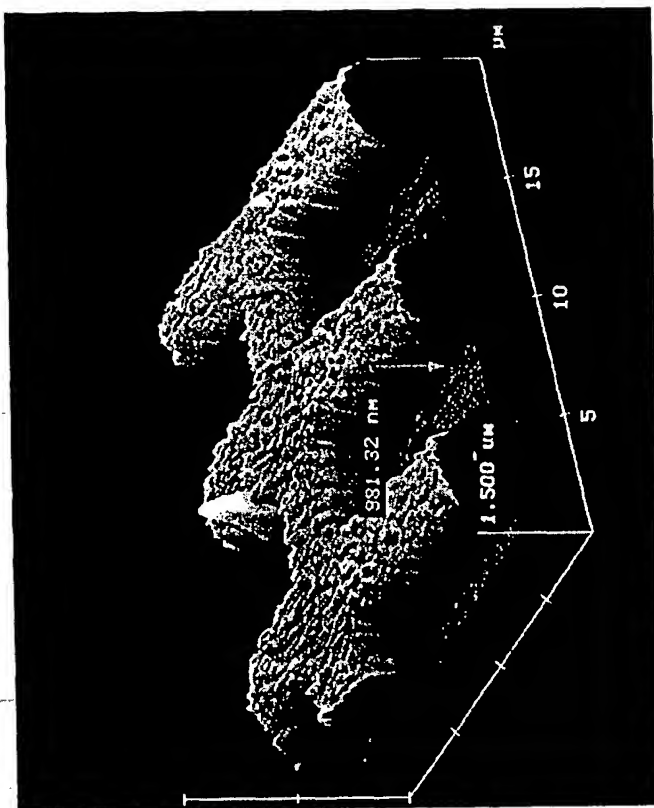


FIG. 1

2/2

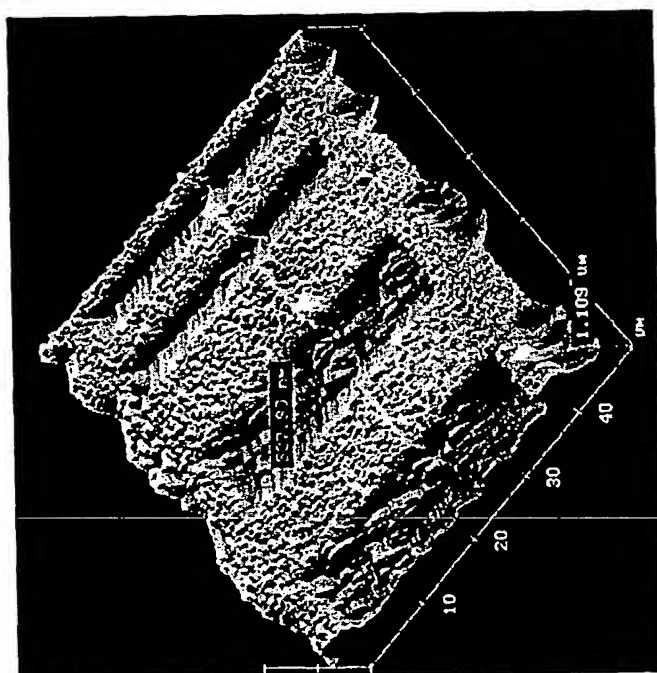
After CO₂ Development



C.HFPO.HF.7
Dose = 10,000 $\mu\text{C}/\text{cm}^2$

FIG. 2B

Before CO₂ Development



C.HFPO.HF.7
Dose = 9,200 $\mu\text{C}/\text{cm}^2$

FIG. 2A

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/01124

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : G03C 5/00

US CL : 430/313,299 ; 216 / 41, 52, 62

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 430/313,299 ; 216 / 41, 52, 62

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,297,401 A (CHERN et al.) 27 October 1981 (27.10.1981), column 2, line 3.	11-14
X	US 5,977,041 A (HONDA) 2 November 1999 (02.11.1999), column 1, lines 20-29; column 1, line 50; column 5, line 38.	1-3, 6, 22-24
Y		4-5, 7, 9-17, 20-21
Y	US 6,013,411 A (AOAI et al.) 11 January 2000 (11.01.2000), column 1, line 5; column 2, line 57.	4, 7
Y	US 6,014,422 A (BOYD et al.) 11 January 2000 (11.01.2000), column 5, line 15.	5
Y	US 5,811,357 A (ARMACOST et al.) 22 September 1998 (22.09.1998), column 2, line 55.	9-10
X	US 5,888,591 A (GLEASON et al.) 30 March 1999 (30.03.1999), column 17, line 33; column 18, line 46.	8, 13
Y	US 5,707,783 A (STAUFFER et al.) 13 January 1998 (13.01.1998), column 3, line 13.	11, 15
Y,P	US 6,020,410 A (HACKER et al.) 1 February 2000 (01.02.2000), column 4, lines 44-50.	11, 16
X	US 5,849,809 A (NARANG et al.) 15 December 1998 (15.12.1998), column 20, line 50.	17-19



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T"

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X"

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y"

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&"

document member of the same patent family

Date of the actual completion of the international search

08 May 2001 (08.05.2001)

Date of mailing of the international search report

21 MAY 2001

Name and mailing address of the ISA/US

Commissioner of Patents and Trademarks
Box PCT
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/01124

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	US 6,149,828 A (VAARTSTRA) 21 November 2000 (21.11.2000), column 3, lines 47-57.	20-21
Y/A	US 5,643,474 A (Sangeeta) 01 July 1997 (01.07.1997), column 4, lines 18-21.	20-21/22-26, 37-39

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/01124

Box I. Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claim Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claim Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
Please See Continuation Sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: 1-26, 37-39

Remark on Protest ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/01124

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I, claim(s) 1-26 and 37-39 drawn to a process requiring at least the steps of depositing a radiation sensitive material on a substrate by chemical vapor deposition, selectively exposing the radiation sensitive material to radiation to form a pattern, and developing the pattern, and to a product that is the product of said process and no other.

Group II, claim(s) 27-34, drawn to a microstructure comprising at least one two-dimensional feature having a tolerance of 7% or less.

Group III, claim(s) 35-35, drawn to a microstructure comprising a three-dimensional structure formed by three-dimensional direct patterning process.

The inventions listed as Groups I-III do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Inventions I and II are related as process of making and product made. The inventions lack unity if the process as claimed is not particularly adapted to making the product. In the instant case, the Group I process requiring at least the steps of depositing a radiation sensitive material on a substrate by chemical vapor deposition, selectively exposing the radiation sensitive material to radiation to form a pattern is not specially adapted to making the Group II product of a microstructure comprising at least one two-dimensional feature having a tolerance of 7% or less.

Inventions I and III are related as process of making and product made. The inventions lack unity if the process as claimed is not specially adapted to making the product. In the instant case, the Group I process requiring at least the steps of depositing a radiation sensitive material on a substrate by chemical vapor deposition, selectively exposing the radiation sensitive material to radiation to form a pattern is not specially adapted to making the Group III product of a microstructure comprising a three-dimensional structure formed by three-dimensional direct patterning process.

Inventions III and II are unrelated. Inventions are unrelated if it can be shown that the special technical feature of the first invention is not present in the second, and that the special technical feature of the second invention is not present in the first. In the instant case the special technical feature of invention II is the microstructure comprising at least one two-dimensional feature having a tolerance of 7% or less. This feature is not present in Invention III. The special technical feature of Invention III is the microstructure comprising a three-dimensional structure formed by three-dimensional direct patterning process, by virtue of not having been formed by three-dimensional direct patterning process. This feature is not present in Invention II.